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XXV.—*On the supposed Existence of Cellulose in Starch-grains.*
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ON no vegetable structure has so great a number of micro-chemical researches been instituted as upon starch-grains; and of none have the structure and chemical composition, in the course of time, been so contradictorily explained. The view of Raspail, that the starch-grain consisted of a vesicular envelope insoluble in water, with soluble gummy contents, was overturned by the researches of Fritzsche and of Payen, who appeared to have demonstrated beyond all doubt that the starch-grain consisted of superimposed layers, formed of one and the same chemical compound throughout the whole thickness of the grain; but Nägeli believed, in his earlier researches at least, that he could discern an outer cellulose membrane,—which opinion was again questioned by myself. Muschke (Journ. f. Prakt. Chemie, lvi. p. 400) still more strongly asserted the presence of cellulose in the starch-grain, thinking he had found the latter to consist of a number of concentric membranes formed of cellulose, between which the starch-substance was deposited, and this in a double modification—one soluble in water, which formed the bright layers of the starch-grain, and one insoluble, of which the dark layers were composed. All these accounts, however, may now be regarded as out of date, since the recent researches of Nägeli ('Die Stärkekörner,' Monographie, 1858) prove indubitably that the whole starch-granule, in all its parts, is composed of two distinct chemical compounds, which in his view form a kind of diffusion †. He arrived at this conclusion

* Bot. Zeitung, July 1st & 8th, 1859; translated by A. Henfrey, F.R.S.

† A very long account of the structure and development of starch has just been published by Trécul in the 'Ann. des Sc. nat.' sér. 4. t. x. It does not contain any new matter of great importance: he advocates the view

by macerating the starch-grains, at a moderate heat (about 104° to 120° F.) in solvent fluids, particularly in *saliva*, which extracted the compound which becomes blue with iodine (the proper starch,) and leaves behind the starch-grains essentially unaltered in their anatomical conditions, but with totally different chemical properties. For the compound dissolved out of the starch he proposes the term *granulose* (p. 209); the remaining substance of the grains is described as cellulose*.

As my critical repetition of Nægeli's observations leads me to regard this last opinion as unfounded, I venture to publish an account of my investigations.

In making the inquiry, I chiefly employed as material the starch of the rhizome of *Canna indica*. For the extraction of the substance coloured blue by iodine I used saliva, because this acts more quickly than extract of malt. The attempt to obtain the same result by organic acids, in the manner described (certainly in no great detail) by Melsens, was unsuccessful. It is necessary to discover by experiment, for each kind of starch, the favourable temperature at which it is to be treated; for at too low a temperature the action does not take place at all, or only very slowly, while too high a temperature produces swelling up and total solution of the granule. In consequence of the latter circumstance, I was less regardful of the maintenance of a constant temperature in the hatching-machine in which I heated the grains than that a certain definite degree of heat should not be exceeded. In the starch of *Canna*, the extraction of the starch-substance began at a temperature of 95° – 104° F., and advanced very slowly and regularly from the periphery of the granule towards its centre, unless it could penetrate by an accidental crack in the granule, in which case the solution in the interior of the granule proceeded rapidly onward from the sides of the crack. At a temperature of 120° – 131° the extraction of the soluble part of the granule was completed in a few hours. A far lower temperature suffices for the extraction of the starch of wheat, while that of potatoes requires a much higher one. If the operation is carried on at a low temperature, the experiment lasting then several days, we must not neglect to pour off

that the layers are formed from without inwards, the older expanding to make room for the new ones.—A. H.

* As often happens, the same discovery of the composition of the starch-grain was made, apparently independently of Nægeli, by Melsens (Institut, 1857, p. 161), who extracted the substance coloured blue by iodine by means of organic acids, diastase, and pepsine, and conjectured that the residue consisted of a nitrogenous substance and another standing near to cellulose. I am unaware whether he has made known his researches in greater detail than in the work here cited.

the saliva daily from the starch-grains, and wash them well, and mix them with fresh saliva, since the putrefactive decomposition of the latter would otherwise ensue, which produces destruction of the starch-grains.

The alterations undergone by the starch-grains are described so accurately by Nägeli that a repetition of the account is entirely superfluous; I confine myself, therefore, to citing the most general features, and to the discussion of those points which appear to me of especial importance for the explanation of the composition of the starch-grain.

The first glance at the starch-grain robbed of its soluble constituent by saliva shows that it has lost considerably in substance, since it possesses far less refractive power; and its much greater mobility in water, and the longer time it takes to settle when stirred up therein, show that it has lost considerably in weight. I could not determine how great this loss of weight is, since this would require a different solvent, which could be removed from the starch-grains entirely by washing, while in the use of saliva many epithelial cells of the lining membrane of the mouth remain mixed up with the granules. The estimate of Nägeli (p. 183), that in potato-starch the mass diminishes from 7 or 8 to 1, may be correct, but it rests upon too insecure a base to be depended upon with certainty.

The magnitude of the grains diminishes far less than the substance; but the amount of decrease is very difficult to state with certainty, on account of the very variable absolute size of the individual grains; and a great number of measurements would be requisite to obtain an approximation to an accurate determination. That a diminution of size does take place, may be very distinctly seen in the starch-grains of germinating wheat, in which the extraction of the soluble substance frequently proceeds, not uniformly from the margin to the centre of the discoid grains, but in separate lines running in the direction of radii, under which circumstance each of these streaks corresponds to a notch or depression at the margin of the grain, which indicates a collapse of the substance towards the interior. Not only, however, is there a contraction of the substance in the radial direction, but there is a still stronger contraction in the direction of the separate laminæ. This is shown very clearly by the behaviour of those grains of *Canna* in which the solution has affected only the outermost layers, when these latter laminæ frequently crack into polyhedral fragments, like dried clay, because the inner and still unaltered laminæ oppose an insurmountable obstacle to their efforts to contract. A still stronger contraction occurs in the laminæ situated between the periphery and the organic centre (likewise in the direction of the laminæ),

as is evident from the circumstance that all the grains of *Canna* from which the soluble substance is entirely removed are traversed by cracks, some tolerably wide, which run out like rays from the centre to the periphery, and are wider in the middle than in the centre and at the periphery, towards which latter they generally thin off;—but when they reach the surface, they frequently cause the grains to fall into sharp-cornered triangular fragments. As these cracks are not connected with the formation of a cavity in the centre of the grain, they do not originate by the inner laminæ becoming contracted in the radial direction with a simultaneous drawing outwards towards the firmer outer layers, causing a lateral extension until they are torn across, but the cracks evidently arise from the contraction of the laminæ of the grains being stronger in the direction of the tangent than in the radial direction.

The lamination undergoes no change by the treatment with saliva. In many cases, particularly when a slow solution of the soluble substance of the grain takes place in the living plant (for example, in germinating wheat), the lamination becomes much more evident in the earlier stages of the process than it was previously, as the solution does not affect all the layers uniformly, but at the outset shows itself only in the looser laminæ, and thereby considerably increases the already existing difference of density of alternating laminæ. But when the soluble portion has been entirely extracted from all the laminæ, and the whole grain has thus acquired far greater transparency, the lamination is mostly far more difficult to perceive than in the fresh grain, as may be seen particularly in the very distinctly laminated grains of the potato.

The substance of the grains which have been exhausted by saliva, so long as they are saturated with water, is in a high degree brittle, and a slight pressure on the covering-glass causes it to crumble into sharp-cornered fragments. When dried, it contracts considerably, which renders the lamination much more indistinct; and a re-wetting with water does not always restore it in the original clearness.

Grains with the starch extracted act upon polarized light exactly like unaltered starch-grains; *i. e.*, when the direction of their laminæ is observed, in the opposite manner to cellulose membranes. In a former paper in this Journal*, on the investigation of vegetable tissues by the aid of polarized light, I regarded this diverse action as the result of a chemical constitution of the starch-grain differing from that of cellulose. The idea might certainly have been entertained that it depended upon conditions of tension in the separate layers of the starch-

* Annals, 3rd series, vol. i. pp. 198, 263.

grain: in this case it would be necessary to assume that there existed in the starch-grain, as in a glass globe whose temperature diminishes from the periphery to the centre, a dilating tension in the radial direction, and a compressing tension in the direction of the surfaces of the concentric laminæ. It might be urged in favour of this, that distinct reasons for the adoption of this view exist in the behaviour of unaltered starch-granules when dried or caused to swell up (as Nägeli thinks it probable, and I believe justly, that in the fresh granules molecules of water contained in them are interposed in greater number in the tangential than the radial molecules of the substance); but we cannot, at all events, conceive such a kind of tension to exist in those granules in which the starch-substance has been extracted from the outer laminæ by saliva, and in which, as above-mentioned, these outer laminæ become torn, by cracks which run in a radial direction, into polygonal fragments, since they cannot contract over the still unexpanded inner laminæ. Here it is beyond doubt that there exists in these outer laminæ an expansive tension in a tangential direction, which rises to the point of fracturing the laminæ, while there is a compressing tension in the radial direction, consequently the reverse of the above assumption. In spite of this, these laminæ freed from starch act in the same manner as unaltered starch-grains. Indeed the optical characters of the grains are not changed by the production of any mechanical alteration in the starch-grains—or by causing, through the action of alcohol or strong desiccation, the formation of a central cavity and the retraction of the internal layers towards the former periphery, combined with tearing in a radial direction—or by causing a swelling up, by which the outer layers then expand, especially in the direction parallel to their surfaces. It therefore appears as though we had here an example of those cases in which the optical phenomena of a body depend, not upon the density and relative distribution of its substance, but upon the quality of the material, like the conditions found by Greilich (*Krystallogr. Opt. Untersuch.* 1858, p. 226) in the comparison of isomorphous compounds of potash and ammonia. In such cases we could not doubt that the optical behaviour of the bodies depended on their intimate molecular conditions. We must, doubtless, recognize this molecular diversity—such as occurs, for example, in the various kinds of sugar—in reference to its effects upon polarized light, first of all as a physical property belonging to them; but, since we have no means of acquiring information regarding the peculiarities of the molecules, and since these peculiarities run parallel with the chemical composition of bodies, I believe I am perfectly justified in assuming that the contrast of negative and positive colours

exhibited by vegetable structures in polarized light stands in connexion with the chemical composition of these structures.

Turning from the consideration of the physical qualities of the starch-grains treated with saliva, to their chemical characters, and looking in the first place to their behaviour with water, we find that they are wholly deprived of the property of swelling up strongly and becoming partially dissolved. It must be premised here, that they are totally destitute of the power of swelling up strongly in water after having been crushed. This is a property of unaltered starch-grains which I think is very little known*. If dried starch-grains, of the potato, for example, are placed on a glass plate, and strongly compressed with a piece of glass of suitable form, so that each grain assumes the form of a flat disk traversed by cracks, and cold water is then added, the flattened grains in the first moment apparently contract, because they first of all swell up again into roundish grains; but they then begin to expand rapidly, as in hot water—less regularly, however, than when they are boiled, often forming pear-shaped curves, evidently because the crushing pressure acts irregularly, and affects one part of the grain more strongly than another. This is particularly evident when a grain has been exposed to strong pressure only on one side, as in this case the crushed part is pushed out in the form of a large, apparently vesicular protuberance, while the remaining part is almost unaffected†. From grains crushed in this way, cold water extracts in solution a portion of the starch-substance, which is coloured blue by iodine, as is seen when solution of iodine is added; for the iodine precipitates the dissolved substance in the form of blue gelatinous pellicles.

The starch-grains treated with saliva are equally destitute of the property of swelling up perceptibly when boiled in water. Their lamination remains as distinct as before, and the angles of cracked grains retain all their sharpness.

If starch-grains, totally deprived of their soluble substance at a tolerably high temperature, are, after thorough cleansing by washing in water, placed in a new portion of saliva, they are found altogether insoluble in it, even when the temperature is

* This swelling-up of crushed grains in cold water appears to have been noticed for the first time by myself, and is mentioned in the article "Starch" in the 'Micrographic Dictionary,' in opposition to the ordinary statement that starch is unaffected by cold water.—A. H.

† This has been explained by myself as a result of the cracks in the resisting outer laminæ allowing access of the water to the more soluble inner substance of the grain. A similar local bulging takes place when weak acid or potash is allowed to run in upon the slide and attack one side of an uncrushed grain.—A. H.

raised to 158° F., at which point unaltered starch-grains are very quickly entirely dissolved.

It is therefore evident that a strong expansive quality exists only in the starch-substance which can be extracted by saliva, and that the intimate combination in which the two substances composing the grains stand in the grains must have a modifying effect upon their respective properties. While the starch-substance is in the fresh grain protected by the substance insoluble in saliva from the solvent action of cold water, when it swells up from the action of hot water, &c., it carries the latter with it in its expansion, and transfers the solution to which it is subject by the action of saliva at a proper temperature, to the substance which in a pure condition is altogether unaffected by saliva.

The substance insoluble in saliva is regarded by Nægeli, as above mentioned, as *cellulose*. In investigating the grounds on which he makes this determination, we must first of all consider the characters which Nægeli uses for distinguishing *cellulose* and *starch*. He says (pp. 182, 189): *The reaction with iodine forms an essential distinction, and at the same time the only discriminative test, between starch and cellulose.* Iodine colours starch, when acting weakly, wine-red or violet; more strongly, indigo-blue or black: pure cellulose, on the contrary, is coloured from pale and dirty reddish to copper-red or reddish brown. Cellulose is, on the other hand, also coloured blue when softened by sulphuric acid, and likewise when saturated with tincture of iodine, dried, and afterwards wetted with water. Since the cellulose is here softened as by sulphuric acid, perhaps iodic or hydriodic acid (or both) may be formed; Nægeli thinks the formation of iodic acid probable. The action of sulphuric acid and the drying up with iodine so transform the condition of aggregation of cellulose, that it behaves like starch with iodine, or, as Nægeli thinks, is converted into starch.

This interpretation of facts, which in themselves are certainly true, is, in my opinion, altogether incorrect. Whether iodine produces a red colour (rising from wine-red, through beautiful purple, to deep violet), or a blue colour (from the brightest sky-blue to deep indigo and apparent black), depends neither on the circumstance that the object is starch or cellulose, nor upon the quantity of iodine, but essentially upon the conditions of the organic substance in respect to water. When very little water is taken up, we have a red, when more, a blue colour. By attending to this point, we may colour cellulose the finest blue, and starch red and violet, without any chemical alteration of the object.

It is self-evident that a greater or less swelling-up of the

organic substance is connected with the absorption of water ; and hence one might be led to find in the capacity of expansion itself a reason for the blue colouring. But this conclusion would certainly not be justified ; for we frequently find that the capability of becoming coloured with iodine does not increase in the same proportion as the capacity for swelling in water, and that, on the contrary, many parts of plants, composed of hydrate of carbon, swelling up strongly in water, are totally destitute of the power of assuming a colour with iodine. On the other hand, a certain degree of absorption of water and expansion is a necessary condition for the absorption of iodine and coloration by it, both with starch and with cellulose, as is simply proved by the circumstance that they remain uncoloured when treated in a dry condition with tincture of iodine prepared with absolute alcohol. Now a substance like starch, when placed, in its natural condition, in contact with water, absorbs such a quantity as allows it to assume a determinate colour with iodine, while another substance must be brought to absorb this water by the simultaneous action of another means, which absorption of water becomes visible to the eye, first of all by enlargement of the volume of the substance, and, with simultaneous action of iodine, by the colour which the latter produces. We are not justified in drawing at once from such an exaltation of the expansive property, and the simultaneously arising alteration of colour by iodine, the conclusion that they depend upon essential chemical changes in the substance, until it has been proved that the other properties of the substance have been altered. This is unproved, more particularly as regards cellulose which has been saturated with tincture of iodine, dried, and re-softened in water ; neither is it proved of cellulose which has been made to swell up in the ammoniacal solution of copper ; on the contrary, this may be perfectly dissolved in the said fluid, and precipitated in an amorphous condition from the solution, retaining all its chemical properties. We see then, on the one hand, that cellulose, without alteration of any chemical properties, absorbs more water under the influence of a material which causes it to swell up than it does in a natural condition, the power of absorbing iodine being simultaneously increased, so that it exhibits the same blue colour which the far more hygroscopic starch exhibits in its natural condition when treated with solution of iodine ; further, starch, on the other hand, when placed in circumstances where it cannot become perfectly saturated with water, exhibits the same colour as cellulose only slightly expanded in water. These circumstances undoubtedly furnish proof that the blue or the red colour is not dependent upon chemical diversity of cellulose and starch, but that particular hydrated conditions of both com-

bine and become coloured in the same way with iodine. The coloration stands altogether on the boundaries between physical and chemical phænomena, and must indeed be connected in the first place with the capacity possessed by various cell-membranes which swell up rather strongly in water, to attract the colouring matter from a solution of carmine in ammonia.

As long as no other means was known by which cellulose could be coloured blue with iodine, except the simultaneous action of sulphuric acid, the conjecture was certainly not far-fetched that this acid transformed the cellulose into starch. Hence this view was many times put forth, for instance by Mitscherlich: I have always regarded it as erroneous, because the cellulose swollen up by means of sulphuric acid has none of the other characters of starch. This assumption is now positively refuted by the researches of Béchamp, who has shown that the subsequent products of the conversion of cellulose by sulphuric acid are essentially different from the corresponding transformation of products of starch, which could not be the case if sulphuric acid converted cellulose in the first place into starch.

Long before this was known, the belief in the conversion of cellulose into starch by sulphuric acid, founded on the blue coloration with iodine, must have been shaken by my demonstrating that the action of sulphuric acid was by no means necessary for the blue coloration of cellulose, but that it sufficed to saturate the cellulose with iodine (which in its usual condition it does not readily absorb) before applying water to it; then, if the cellulose is made to absorb water, the iodine renders it blue, until itself is completely extracted again by the water surrounding the preparation. Nägeli endeavours to explain this process also by a chemical conversion of the cellulose; for he conjectures that the iodine gives origin to iodic and hydriodic acids, which transform the cellulose. This is an entirely arbitrary and groundless hypothesis. It should at least have been demonstrated by experiment that these acids have the power of acting in the same manner upon cellulose as sulphuric acid, and of producing a blue colour in it in the presence of iodine. I have made the experiment of saturating purified cellulose with tincture of iodine, and adding the said acids; they caused neither a visible action upon the cellulose nor a trace of blue coloration.

But, without this demonstration that the said acids do not bring about a conversion of the cellulose and its blue coloration, it may be recognized from the behaviour of the cellulose saturated with iodine, that it is not transformed into starch. Iodine affects starch infinitely more readily than it does cellulose, so that starch absorbs the iodine out of water when only a minimum

of iodine is contained in the latter. At the same time the iodine adheres very firmly to starch, so that repeated washings with much water are required to extract the iodine from blued starch. It is quite different with cellulose saturated with iodine : it certainly also very quickly becomes blue when water is added, for it already contains the iodine ; but it retains the latter with very little power, and quickly parts with it to the surrounding water. The cellulose bleached in this way is just as difficult to colour blue with iodine a second time, and takes up as little from an aqueous solution as cellulose which has never been in contact with iodine. If the saturation with iodine had caused the conversion of even a small portion of it into starch, the behaviour must have been essentially different.

The same conclusion, that the blue colouring of cellulose does not depend upon the previous formation of starch, may be drawn from the phenomena which are exhibited by cellulose under the action of chloride of zinc and iodine. I used for these experiments, on the one hand, tissues which had been purified by the known method of Schulze, by boiling with a mixture of nitric acid and chlorate of potash,—on the other hand, cellulose in an amorphous condition, which had been prepared by my colleague Schlossberger by precipitating a solution of cotton in ammoniacal solution of copper by adding common salt. The reaction of both modifications with iodine was perfectly identical. The cellulose, brought in a dry condition into contact with the viscid solution of chloride of zinc, absorbed from it so little water that it did not perceptibly swell up with it*. At the same time there was no trace of blue colouring. The colour is always some tint of red in wood-cells and vessels, in cellulose precipitated from ammoniated oxide of copper more purple or brown-red, approaching more to violet in parenchymatous cells. If the preparation saturated with iodine is now placed in water, the colour turns suddenly to blue, and very often, especially in the precipitated cellulose, to the finest indigo-blue. Yet the iodine is not firmly retained under these circumstances, but is washed out by water just as rapidly as out of cellulose with which the iodine has been incorporated by saturating with the tincture. If the chloride of zinc had caused a chemical

* This will be seen most clearly from the following experiments. It is well known that the leaves of many mosses roll up when dried, and spread out again when they absorb water. I laid stems of *Bartramia pomiformis* thus dried in the solution of chloride of zinc; but at the end of three days their leaves were as strongly rolled up as at first, although they had become somewhat more transparent; the membrane of their cells had therefore absorbed a smaller quantity of water than it contained in the natural condition of the fresh plant. When I transferred the plants from the solution of chloride of zinc into water, their leaves unfolded immediately.

conversion of the cellulose, and this had led to the production of the blue colour, it must have been rendered evident by drying this cellulose, which had been saturated with water and coloured blue, and driving off the iodine by gentle heating. If the cellulose had been converted into starch, this could not be removed from the preparation by drying, and the blue colour would necessarily make its appearance on the wetting with tincture of iodine. But this does not take place; for the cellulose behaves exactly as before—is coloured red with chloride of zinc, &c. Moreover, if cotton is treated with the ammoniated oxide of copper, yet not exposed to its action long enough to produce solution, but only until the filaments have become swollen up, the latter are coloured blue by tincture of iodine after having been well washed out with water. Under this influence of the ammoniacal solution of oxide of copper, the cellulose has acquired the property of absorbing more water than it can in its natural condition; but that we cannot imagine any conversion into starch in this case, follows from the previously mentioned circumstance, that the cellulose does not undergo this change even after complete solution, but may be precipitated with all its properties by salt.

Summing up what has been stated, it becomes evident that the blue coloration of cellulose by iodine by no means furnishes proof that the former is wholly or partly converted into starch, but that its blue colour depends solely upon the circumstance that cellulose absorbs simultaneously iodine and a sufficient quantity of water, while, with a smaller absorption of water, the red tints are produced.

Just as we are able to impart a pure blue colour to cellulose saturated with iodine by merely adding water, we can, on the other hand, by suitable operations, impart to the starch-grains the property of becoming coloured red, and not blue, with iodine. And in this case the red or blue colour depends, not upon the quantity of iodine which we incorporate with the starch, but upon the water contained in the latter.

If we place potato-starch in water, in which it is well known to become rapidly saturated, its grains begin to assume colour with the addition of a minimum of iodine; but if little iodine is applied, so that only part of the grains are coloured, and these very slightly, no red colour is produced, but the colour, if not bright, is still decidedly blue. Very different results ensue from adding an excess of iodine to the starch, allowing at the same time only slight absorption of water. If, for example, we place dry potato-starch in a solution of cane-sugar concentrated to the crystallizing point (which, from its great power of attracting water from organic bodies, gives very little water

to the starch-grains), and add tincture of iodine, the starch-grains do not become blue, but are coloured various tints, from bright wine-red to violet. The colours change to blue directly water is applied. The same result is obtained when dried potato-starch is placed in absolute alcohol, a considerable quantity of iodine dissolved in this, and water dropped in carefully and with frequent agitation, until the starch-grains are coloured: their colour will be from reddish to deep violet, but none will appear blue. A greater addition of water at once brings out the blue colour.

Analogous phænomena are displayed during the action of chloro-iodide of zinc upon dry starch. The latter is capable of abstracting water from the solution, and gradually becomes strongly swollen up through the influence of chloride of zinc. But this process requires much time; and the outermost layer of the granules especially opposes at first a resistance to the expansion. Hence the grains appear at first brown-red, like dry starch-grains saturated with iodine; subsequently this colour changes while they swell up (which often occurs irregularly and partially), into a bright blue. If, however, the quantity of the starch in proportion to the chloride of zinc solution is great, and, after complete swelling-up, forms with it a very tough, dense, and glutinous mass, the bright blue colour changes in the course of twenty-four or thirty-six hours, during the swelling-up and while the toughness of the mass increases, into a fine purple-red. If water is now added without fresh iodine, the colour changes rapidly into blue. Here evidently, at the commencement of the swelling-up of the grains, the quantity of water in the zinc solution is sufficient to supply the half-swollen granules with enough water for the production of the blue colour, while with the increasing expansion of the starch-grains it becomes again insufficient, and thus the blue colour is brought back to red.

If I have rightly comprehended the above-described phænomena, the reaction of cellulose and starch with iodine, far from being the only test by which to distinguish them, affords, *on the contrary, a character of no value for distinguishing between the two chemical compounds.*

Strictly speaking, Nægeli did not regard the colour which the said substances take with iodine as the only distinction between them; for he mentions as a second the circumstance that cellulose withstands solvents more strongly than starch, while starch-grains, on account of the cellulose they contain, are caused to swell up and dissolve with more difficulty than pure starch would be (p. 193). This statement is certainly true in respect to most solvents, and the complete insolubility of cellulose in water must

above all be brought forward as a distinctive character; it is, however, not universally valid. Ammoniated oxide of copper dissolves purified cellulose very quickly; but, so far as my experience goes, it is quite incapable of dissolving a starch-grain, only causing it to swell up. Another solvent for cellulose, which cannot dissolve starch, is the ferment in putrefying potatoes, discovered by Mitscherlich. Nägeli thinks the action of this upon cellulose must be attributed to its setting up decomposition in the proteine substances contained in the cell-membranes, and carrying this over to the cellulose, while, as the starch contains no proteine, it does not become decomposed. It is probable that this may be the true explanation; but, before we can admit it as correct, it must be proved by comparative observations on the action of this ferment upon purified cellulose and starch. I have no experience on this point.

If we agree with Nägeli in regarding that portion of the starch-grain insoluble in saliva as cellulose, we may name a number of other substances which dissolve cellulose but not starch-grains. In any case, it is a partial view to deduce the insolubility or the difficult solubility of starch-grains from the insolubility of the substance insoluble in saliva contained in them, since, on the other hand, this latter substance in a purified condition is very readily dissolved by many materials, while in the starch-grain it is protected from their solvent action by its combination with starch.

From what is above related, I find it impossible to admit that Nägeli has conceived the distinctions between cellulose and starch according to nature; still less am I convinced that he has arrived at proof of the view that the substance left of the starch-grains after the removal of the soluble part by saliva is identical with cellulose. The following facts will show that this substance behaves differently, with a number of reagents, from purified cellulose.

The grounds upon which Nägeli here rests lie especially in the reaction of this substance with iodine (p. 186), its assuming a copper-red or red-brown colour with aqueous solution of iodine, tincture of iodine, or iodide of zinc, and a blue colour when dried up with tincture of iodine and wetted with water, or treated with iodine and sulphuric acid.

The characters certainly indicate a great similarity to cellulose. I may mention, as a further agreement, that ammoniated oxide of copper dissolves both substances. But let us look at the differences.

In regard to physical properties, it must be observed that the substance of starch-grains is very brittle, while pure cellulose is perceptibly tough; further, that, as above-stated, the two substances act in opposite ways on polarized light.

In reference to the chemical reactions, I met with the following distinctions, in detailing which I shall, for the sake of brevity, simply use the terms *starch-grains* and *cellulose*, without especially mentioning that in each case I refer to starch-grains exhausted by saliva, and cellulose purified by Schulze's method.

Solution of caustic potash dissolves the starch-grains suddenly; cellulose swells up in it, but remains undissolved after many hours.

Solution of chloride of zinc and iodine, when concentrated, dissolves starch-grains instantly into a brownish-red fluid; cellulose does not swell perceptibly in it, and resists solution for days.

Ammoniated oxide of copper, to which so much carbonate of ammonia has been added that it will no longer act upon cellulose, dissolves the starch-grains instantly; when still more carbonate of ammonia is added, the starch is no longer dissolved.

Ammoniated oxide of nickel dissolves the starch-grains instantly; but cellulose is insoluble in it.

Nitric acid dissolves the starch-grains instantly; but cellulose bears long boiling in this acid mixed with chlorate of potash.

Hydrochloric acid dissolves the starch-grains immediately; cellulose is not perceptibly attacked by this acid.

Among these diversities, the different behaviour with polarized light forms the sharpest contrast; the other differences might be regarded rather as gradual, since they all agree in showing that the substance contained in the starch-grains is soluble in a number of media in which cellulose is only slightly or not at all soluble. Hence a question might be raised whether these diversities were sufficiently great to warrant the conclusion that the substance of the starch-grains is different from cellulose. In regard to this it must be fully borne in mind, in reference to the distinctions between the two substances relating to their solubility in many of the media named, especially in ammoniacal oxide of nickel, chloro-iodide of zinc, nitric and hydrochloric acids, that I tested the behaviour with these media of purified cellulose derived from a considerable number of plants which exhibited no important differences whatever in the behaviour of the membranes; so that these differences are as constant and striking as the difference between the various kinds of sugar.

If therefore we desire to distinguish from one another the hydrates of carbon of which the organic structures of plants are composed, by such reactions, there is abundant ground against ranging the substance of starch-grains exhausted of starch with cellulose, and for giving it a proper name (say *farinose*). However, I will not in this respect forestall the chemists, before whom the whole matter must come for definitive settlement.

Tübingen, February, 1859.